SCIENTIFIC PAPERS

OF THE

BUREAU OF STANDARDS

GEORGE K. BURGESS, Director

VOLUME 19

1923–24

CONTENTS OF VOLUME 19

INVESTIGATIONS ON THE PLATINUM METALS

IV. DETERMINATION OF IRIDIUM IN PLATINUM ALLOYS BY THE METHOD OF FUSION WITH LEAD

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February 28, 1924

INVESTIGATIONS ON THE PLATINUM METALS [1]

IV. DETERMINATION OF IRIDIUM IN PLATINUM ALLOYS BY THE METHOD OF FUSION WITH LEAD.

By Raleigh Gilchrist.

ABSTRACT.

A study has been made of the analytical details of the Deville and Stas method for the determination of iridium in platinum alloys containing from 0.1 to 20 per cent of iridium. Specially prepared alloys made from highly purified metals were used in the investigation. It was found that the concentration of nitric acid, the concentration of aqua regia, the proportion of lead, and the time and the temperature of the lead fusion can be varied over a wide range without affecting the determination. The observations of Deville and Stas that palladium and rhodium have no effect upon the determination and that ruthenium separates quantitatively with the iridium were confirmed. In addition, gold was found not to interfere. Iron separates nearly quantitatively with the iridium as observed by Deville and Stas. A method for the separation of iron from the iridium was tested and found to give satisfactory results. The loss in weight of crystalline iridium during the ignition periods is insignificant and the weight of crystalline iridium is not affected by heating and cooling in an atmosphere of hydrogen. Spectrographic examination of samples of iridium from analysis showed that neither platinum nor lead was present in sufficient quantities to affect the determination. The iridium results tend to be low by a variable but usually small amount. One factor in this error is a slight solution of iridium by aqua regia. A modified procedure for the method is offered, which combines the optimum conditions for speed and accuracy in the various details of manipulation.

CONTENTS.

[1] (I) The preparation of pure platinum, by Edward Wichers, J. Am. Chem. Soc., 43, p. 1268; 1921; (II) Investigations on platinum metals at the Bureau of Standards, by Edward Wichers and Louis Jordan, Trans. Am. Electrochem. Soc., 43, p. 385; 1923; (III) The preparation of platinum and of platinum-rhodium alloy for thermocouples, by R. P. Neville, Trans. Am. Electrochem. Soc., 43, p. 371; 1923.

I. INTRODUCTION.

The determination of iridium in platinum alloys by the method of fusion with lead was devised by Deville and Stas [2] about 50 years ago. Since that time no critical investigation of the method has been made to determine its reliability and accuracy. This method is the one most commonly used for the determination of iridium.

As iridium alloys are now widely used commercially, it is important that a precise and dependable method for the analytical determination of iridium be known. Consequently, a critical study of the Deville and Stas method was undertaken at the Bureau of Standards as the first of a series of investigations into the analytical methods for the metals of the platinum group. The range 0.1 per cent to 20 per cent was chosen for investigation. The lower limit represents platinum of commercial purity, while alloys containing a proportion of iridium greater than 20 per cent are seldom used commercially.

II. THE DEVILLE AND STAS METHOD.

The directions given by Deville and Stas [3] for the analysis of the alloy containing 10 per cent of iridium and 90 per cent of platinum used in the manufacture of the standard meter are embodied in the report of the French section of the International Committee of Weights and Measures.

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[2] Procès-verbaux, Comité International des Poids et Mesures, 1877, p. 185.

[3] Loc. cit.

In his researches on platinum-iridium alloys Deville [4] discovered that when he dissolved in lead at a high temperature platinum alloyed with iridium, rhodium, palladium, iron, and copper he was able to effect a very distinct separation of the platinum metals. The lead formed alloys with all of the platinum, rhodium, palladium, and copper and with a very small proportion of the iron. The iridium, ruthenium, and iron formed a separate alloy containing no lead. Boiling dilute nitric acid removed the bulk of the lead, together with the palladium and copper and a small proportion of the platinum and rhodium. Digestion of the residue with warm dilute aqua regia left insoluble only the alloy of iridium, ruthenium, and iron.

The procedure used by Deville and Stas for the analysis of the ends of the platinum-iridium bars Nos. 3 and 6 was as follows:

Five grams of the laminated alloy was fused with 50 g of pure lead for a period of four hours at a temperature approximating the melting point of gold. The fusion was made in a covered crucible of purified carbon which was set within a porcelain crucible, the space between being filled with fragments of wood charcoal. The cooled lead ingot was placed in an evaporating dish containing 400 cc of boiling water. Just enough nitric acid was added from time to time to cause the evolution of gas until no more lead dissolved. The residue was treated with warm aqua regia made from 4 volumes of concentrated hydrochloric acid and 1 volume of nitric acid (sp. gr. 1.3) diluted with 9 volumes of water. The residue, insoluble in the dilute aqua regia, was caught on a filter, washed thoroughly, ignited, reduced to the metallic state by illuminating gas, and weighed. The reduced metal was fused with potassium hydroxide and nitrate in a gold crucible at dull red heat for three hours. The alkali fusion was taken up in water and the ruthenium removed as the volatile tetroxide in a current of chlorine. The contents of the distilling flask were then evaporated to dryness and taken up in water. Sodium hydroxide and alcohol were added and the solution heated to boiling to precipitate all of the iridium and iron. The iridium and iron oxides, separated from the solution by filtration, were strongly ignited in a platinum crucible. The ignited oxides were digested with ammonium iodide solution, strongly acidified with hydrochloric acid, to remove iron, while gold introduced during the fusion was eliminated by chlorine water and silica was removed by a treatment with hydrofluoric acid. The iridium, thus freed of impurities, was finally reduced to the metallic state by means of illuminating gas, in which condition it was weighed.

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[4] Loc. cit., p. 162.

The Deville and Stas procedure has been used at the Bureau of Standards for the past six years, but with a few modifications in apparatus and technic. The crucible used for the fusion was machined from Acheson graphite with the inside slightly tapered to facilitate the removal of the cooled lead ingot. An electrically heated furnace, made by winding nichrome resistance wire around a deep alundum cylinder, was used. In such a furnace, covered with a piece of asbestos, a temperature of about 1,000° C. was readily maintained with very little combustion of the graphite. Instead of adding the nitric acid in small portions the lead button was digested in nitric acid of the strength 1 volume of concentrated nitric acid to 8 volumes of water in an Erlenmeyer flask at about 85° C. Aqua regia of slightly different concentration was used, namely, 1 volume of mixed acid to 10 volumes of water. The acids had the ratio 6 volumes of hydrochloric acid (sp. gr. 1.18) to 1 volume of nitric acid (sp. gr. 1.42). Hydrogen, instead of illuminating gas, was used to reduce the iridium to the metallic state.

In some laboratories the lead fusion is made on charcoal before the blowpipe.[5] The sample is wrapped in at least 10 times its weight of sheet test lead and placed in a flat depression in a stick of wood charcoal, where it is fused for a minute or so at a dull-red heat. The molten button is constantly rotated. This procedure is limited to rather small samples. If a large sample is to be analyzed, it must be divided into a number of portions, which are fused separately. In another laboratory the fusion is made in a smoked porcelain crucible over a Bunsen burner for about three hours, the temperature not exceeding 800° C.[6] In still another laboratory the alloy is scorified with lead.[7] No comparative tests of these methods have been made in this laboratory.

III. DETAILS OF THE ANALYSIS MADE THE SUBJECT OF INVESTIGATION.

In order to arrive at the optimum conditions for the determination of iridium in platinum alloys, a study was made of the following details: Magnitude of the error caused by incomplete separation of iridium; variation of the concentration of nitric acid and of aqua regia used; variation of the proportion of lead to alloy and of the time and temperature of the lead fusion; effect of

[5] Private communications from Paul R. Heyl and A. M. Smoot.
[6] Private communication from T. A. Wright.
[7] Private communication from H. E. Holbrook.

ruthenium, rhodium, palladium, gold, and iron; and the effect of ignition in air and of reduction in hydrogen on the weight of crystalline iridium.

IV. PREPARATION OF ALLOYS FOR ANALYSIS.

The alloys were specially prepared for this investigation from metals of the highest purity. The platinum had been prepared for use in thermocouples, and its spectrum showed only a trace of calcium. The iridium had been fused with lead, and its spectrum showed the presence of traces of platinum, rhodium, ruthenium, lead, and iron, so small, however, that they could have no appreciable effect on the composition of the alloys. The palladium was free from base metals, while the rhodium sponge may have contained a trace of lead, but both were free from the other platinum metals. The spectrum of the gold indicated a trace of silver and copper.

The alloys were melted in an Ajax-Northrup high-frequency induction furnace,[8] using pure lime or purified thoria as the refractory. The platinum used was either in the form of an ingot or of wire pressed into a pellet in a steel mold. Platinum sponge was not used, because it could not be melted in the induction furnace unless previously compressed and because it always contained a small proportion of volatile matter, which caused a variable loss of weight on melting. In order to add the finely crystalline iridium without loss, it was wrapped in a small cylindrical shell made of pure platinum foil. The molten alloys were stirred vigorously by the effect of the induced electric current. With the exception of the iron-iridium alloy, which was cast in graphite, the melts were allowed to freeze in the crucibles.

Preliminary experiments showed that pure platinum could be melted without significant loss in weight. In the melting of iridium alloys, however, there was always some loss in weight. On the basis of these experiments the loss in weight observed in melting the alloys used in this investigation was regarded as a loss of iridium. Iridium is known to volatilize more rapidly than platinum, probably as an oxide.

Early analyses indicated the necessity of careful sampling because of the nonhomogeneity of some of the alloys. In the first attempt that was made to procure a uniform sample the ingot (containing 20 per cent iridium) was rolled and drawn into wire

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[8] R. P. Neville, The preparation of platinum and of platinum-rhodium alloy for thermocouples, Trans. Am. Electrochem. Soc., **43**, p. 371; 1923.

of 0.60 mm diameter. The wire was cut into fragments varying from 1 to 2 mm in length. Results of analysis of this alloy showed that still greater care should be taken. With all the alloys made subsequently, the wire was drawn to 0.36 mm and cut into lengths of 1 mm. The cut wire in every case was thoroughly cleaned of superficial iron by means of hot concentrated hydrochloric acid, washed with distilled water, and ignited to dull redness in a porcelain crucible. Samples for analysis were taken from different parts of the mass.

Two limiting values for the percentage of iridium are given in most of the tables. The "maximum percentage of iridium" is the percentage of iridium in the mixture before melting. The "minimum percentage of iridium" is the value calculated after melting, if the loss in weight is regarded as a loss of iridium. The lower limiting value, in all probability, represents more closely the average iridium composition of the alloys. The weights of the different alloys prepared for analysis varied from 15 to 45 g.

V. RESULTS OF THE ANALYSES.

1. DANGER OF NONUNIFORM SAMPLING.

Eight analyses were made on 2 g samples of an alloy containing a maximum of 20.00 per cent of iridium and a minimum of 19.83 per cent. The average of the determinations was 19.85 per cent, but the individual results varied from 19.51 to 20.34 per cent.

Five analyses were made on 2 g samples of an alloy containing a maximum of 8.64 per cent of iridium and a minimum of 8.57 per cent, and, in addition, 8.5 per cent of rhodium. The average of the determinations was 8.77 per cent, but the individual results varied from 8.49 to 9.02 per cent.

The samples of the two alloys mentioned consisted of single pieces of fairly heavy rod or wire. The variation in analytical results led to the belief that this method of sampling was inadequate. A change in the method of sampling adopted in subsequent analyses confirmed this belief.

2. INCOMPLETE DETERMINATION OF IRIDIUM.

Early in the experimental work iridium was detected qualitatively in the aqua regia solution. Although the amount in this case was small, it was evident that some iridium was being lost. In order to determine the magnitude of this error, iridium was recovered from the aqua regia solutions in the analyses of a number of the alloys. The recoveries were made in this way: The

total aqua regia solution was evaporated to dryness in a porcelain casserole on the steam bath. Nitric acid was destroyed by repeated evaporations with hydrochloric acid. Ammonium chloride in slight excess was added to the aqueous solution and the mass of salt dried as thoroughly as possible on the steam bath. The dried salt was transferred to a porcelain crucible and decomposed in an atmosphere of hydrogen. The ignited metal was transferred to a graphite crucible with the aid of an ashless filter and fused with lead, as in the regular procedure for an alloy.

In reporting the analyses in which this second determination of iridium was made the total iridium is the value which is considered in the discussion of the results, but the weights obtained in the two determinations are tabulated separately. Iridium was recovered from the aqua regia solutions in 33 experiments. Calculated in percentage on the basis of the weight of the alloy samples taken, 20 were less than 0.05 per cent, 7 were between 0.05 and 0.10 per cent, 4 were between 0.10 and 0.15 per cent, and 2 were between 0.15 and 0.30 per cent.

There was no uniformity in the quantity of iridium which escaped the first determination, considering either individual experiments or the averages from different alloys, although these alloys differed considerably in iridium content. It is difficult, therefore, to draw conclusions as to the causes of this error. Iridium which is filtered from the aqua regia solutions is always in the form of very fine crystals, the density of which probably approaches that of compact iridium, about 22.5. The error caused by incomplete transfer to the filter or by the passage of some of the finely divided metal through the paper would accordingly be comparatively large. However, it seems unlikely that more than a very small quantity could have been involved in a mechanical loss of this sort, since the utmost precautions were taken to effect a quantitative transfer and a double filter was used, both layers of which were of paper of close texture. There was probably some solution of the iridium by the aqua regia in all cases, but the reason why the amount dissolved should vary between wide limits is not apparent. As stated, the error is not proportional to the amount of iridium in the alloy nor was it found to vary regularly with the concentration of the aqua regia used. Although the error may not be of concern in ordinary commercial analysis, especially if duplicate or triplicate determinations are made, it is clear that a recovery of iridium from the aqua regia solution should be made if the greatest accuracy is desired.

3. EXPERIMENTS ON THE VARIATION OF THE CONCENTRATION OF NITRIC ACID USED TO DISINTEGRATE THE LEAD BUTTON.

Table 1 illustrates the accuracy which is possible when sampling is properly done. Under the heading "Conditions" in the tables are given the details of treatment of the alloys during analysis; for example, "10 lead" means that 10 parts of granular test lead to 1 part, by weight, of alloy were used in the fusion. The temperature of the lead fusion is next given with the time of fusion in parentheses. The concentration of the nitric acid is given as a ratio; for example, 1 : 8 signifying that 1 volume of nitric acid (sp. gr. 1.42) was diluted with 8 volumes of water. The figure 1 : 10 aqua regia means that 1 volume of mixed acid was diluted with 10 volumes of water. The acids had the ratio 6 volumes of hydrochloric acid (sp. gr. 1.18) to 1 volume of nitric acid (sp. gr. 1.42). The figures in parentheses adjacent to the acid concentrations give the time of digestion with the acids named. In all this work the temperature of the acid solutions was maintained at about 85° C. A double filter was always used.

The results given in Table 1 show that the concentration of the nitric acid can be varied over a wide range without affecting the determination. The results given in Table 8 further confirm this observation.

Disintegration of the lead button was accomplished by 1 : 2 nitric acid in less than two hours, leaving the residue, however, in a finely divided condition troublesome for filtering and washing. With 1 : 4 nitric acid the time required was two hours, while with 1 : 8 nitric acid complete disintegration could scarcely be accomplished in one working day. There was no difference in appearance between the residues obtained in these two cases.

In all of the experiments the same quantity of nitric acid (sp. gr. 1.42) was used with a varying quantity of water. Before filtering it was necessary to dilute the stronger acid solutions to the volume of the 1 : 8 concentration in order to prevent recrystallization of lead nitrate.

4. EXPERIMENTS ON THE VARIATION OF THE CONCENTRATION OF AQUA REGIA USED TO SEPARATE THE IRIDIUM FROM THE LEAD-PLATINUM ALLOY.

The results given in Table 2 show that variation of the concentration of the aqua regia has little or no effect. This is the alloy which was drawn to wire of 0.60 mm diameter instead of to 0.36 mm. Such variations as appear in the results are probably to be ascribed to somewhat inadequate sampling rather than to the variation of the concentration of the aqua regia. While with 1 : 10 aqua regia complete separation could not be

accomplished in one working day, with 1 : 2.5 aqua regia it could be done within one and one-half hours. That the 1 : 2.5 concentration did give consistent results is illustrated in the analysis of alloy No. 141, Table 8, and of alloy No. 104, Table 5, Series IV.

The variation in the concentration of the aqua regia was made by altering the quantity of water. It was necessary to dilute the stronger acid solutions to the volume of the 1 : 10 acid before filtration in order to prevent the separation of lead chloride.

TABLE 1.—Variation of the Concentration of Nitric Acid.

Alloy No. 132 {Maximum percentage of Ir=4.85.
{Minimum percentage of Ir=4.82.

SERIES I (1 : 8 NITRIC ACID).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Percentage of Ir.	Conditions.
	g	g		
1.............	4.0024	0.1934	4.83	10 lead; 1,000° C. (1½ hours); 1 : 8 nitric acid (19 hours);
2.............	4.0011	.1934	4.83	1 : 10 aqua regia (23 hours).
3.............	4.0020	.1933	4.83	
Average..	....	....	4.83	

SERIES II (1 : 4 NITRIC ACID).

1.............	4.0018	0.1935	4.83	10 lead; 1,000° C. (1½ hours); 1 : 4 nitric acid (19 hours);
2.............	4.0020	.1940	4.85	1 : 10 aqua regia (23 hours).
3.............	4.0011	.1933	4.83	
Average..	....	....	4.84	

SERIES III (1 : 2 NITRIC ACID).

1.............	4.0015	0.1917	4.79	10 lead; 1,000° C. (1½ hours); 1 : 2 nitric acid (3 hours);
2.............	4.0009	.1921	4.80	1 : 10 aqua regia (23 hours).
Average..	....	....	4.80	

TABLE 2.—Variation of the Concentration of Aqua Regia.

Alloy No. 101 {Maximum percentage of Ir=20.20.
{Minimum percentage of Ir=20.11.

SERIES I (1 : 10 AQUA REGIA).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
	g	g	g	g		
1.............	2.0036	0.3986	0.0016	0.4002	19.97	20 lead; 1,000° C. (4 hours); 1 : 8 nitric acid
2.............	2.0089	.4016	.0008	.4024	20.03	(23 hours); 1 : 10 aqua regia (23 hours).
3.............	2.0054	.3967	.0042	.4009	19.98	
Average....	....	....	....	....	19.99	

SERIES II (1 : 5 AQUA REGIA).

1.............	2.0022	0.4010	0.0018	0.4028	20.12	20 lead; 1,000° C. (4 hours); 1 : 8 nitric acid
2.............	2.0011	.3988	.0025	.4013	20.05	(23 hours); 1 : 5 aqua regia (23 hours).
Average....	....	....	....	....	20.09	

SERIES III (1 : 2.5 AQUA REGIA).

1.............	2.0029	0.3981	0.0026	0.4007	20.01	20 lead; 1,000° C. (4 hours); 1 : 8 nitric acid
2.............	2.0043	.4003	.0028	.4031	20.11	(23 hours); 1 : 2.5 aqua regia (23 hours).
Average....	....	....	....	....	20.06	
Grand av...	....	....	....	....	20.04	

5. EXPERIMENTS ON THE VARIATION OF THE DURATION OF THE LEAD FUSION.

The results given in Table 3 show that the time of fusion, with the temperature at 1,000° C., may vary over a wide range without seriously affecting the determination.

TABLE 3.—Variation of the Duration of the Lead Fusion.

Alloy No. 101 {Maximum percentage of Ir=20.20.
{Minimum percentage of Ir=20.11.

SERIES I (4 HOURS).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
	g	g	g	g		
1.............	2.0036	0.3986	0.0016	0.4002	19.97	20 lead; 1,000° C. (4 hours); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	2.0089	.4016	.0008	.4024	20.03	
3.............	2.0054	.3967	.0042	.4009	19.98	
Average....	....	....	....	....	19.99	

SERIES II (2 HOURS).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
1.............	2.0052	0.4008	0.0005	0.4013	20.01	20 lead; 1,000° C. (2 hours); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	2.0065	.4027	.0003	.4030	20.08	
Average....	....	....	....	....	20.05	

SERIES III (1 HOUR).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
1.............	2.0031	0.4021	0.0010	0.4031	20.12	20 lead; 1,000° C. (1 hour); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	2.0049	.4028	.0000	.4028	20.09	
Average....	....	....	....	....	20.11	

SERIES IV (ONE-HALF HOUR).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
1.............	2.0034	0.3994	0.0027	0.4021	20.07	20 lead; 1,000° C. (one-half hour); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	2.0022	.4003	.0008	.4011	20.04	
Average....	....	....	....	....	20.05	
Grand av...	....	....	....	....	20.04	

6. EXPERIMENTS ON THE VARIATION OF THE PROPORTION OF LEAD TO ALLOY.

The results tabulated in Table 4 show that the proportion of lead can be varied over a wide range without appreciably affecting the determination.

TABLE 4.—Variation of the Proportion of Lead to Alloy.

Alloy No. 101 { Maximum per centage of Ir=20.20.
{ Minimum percentage of Ir=20.11.

SERIES I (10 LEAD).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
	g	g	g	g		
1............	2.0042	0.3967	0.0059	0.4026	20.09	10 lead; 1,000° C. (4 hours); 1 : 8 nitric
2............	2.0060	.3994	.0018	.4012	20.00	acid (23 hours); 1 : 10 aqua regia (23 hours).
Average....					20.05	

SERIES II (20 LEAD).

1............	2.0036	0.3986	0.0016	0.4002	19.97	20 lead; 1,000° C. (4 hours); 1 : 8 nitric
2............	2.0089	.4016	.0008	.4024	20.03	acid (23 hours); 1 : 10 aqua regia (23 hours).
3............	2.0054	.3967	.0042	.4009	19.98	
Average....					19.99	

SERIES III (40 LEAD).

1............	2.0048	0.4022	....	0.4022	20.06	40 lead; 1,000° C. (4 hours); 1 : 8 nitric
2............	2.0058	.4007	....	.4007	19.98	acid (23 hours); 1 : 10 aqua regia (23 hours).
Average....					20.02	
Grand av...					20.02	

7. EXPERIMENTS ON THE VARIATION OF THE TEMPERATURE OF THE LEAD FUSION.

The results in Table 5 show that the temperature may vary between 800 and 1,000° C. without seriously affecting the determination. However, it appears that a short fusion at 800° C. is not sufficient.

TABLE 5.—Variation of the Temperature of the Lead Fusion.

Alloy No. 104 {Maximum percentage of Ir=10.26.
{Minimum percentage of Ir=10.22.

(Series I (600° C.).—Unsatisfactory; fusion incomplete.)

SERIES II (800° C. FOR ONE-HALF HOUR).

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
	g	g	g	g		
1.............	1.3496	0.1384	0.0001	0.1385	10.26	10 lead; 800° C. (one-half hour); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	1.3496	.1396	.0000	.1396	10.34	
Average....	....	....	....	....	10.30	

SERIES III (800° C. FOR 4 HOURS).

1.............	1.3549	0.1367	0.0013	0.1380	10.18	10 lead; 800° C. (4 hours); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (23 hours).
2.............	1.3330	.1340	.0010	.1350	10.13	
Average....	....	....	....	....	10.16	

SERIES IV (1,000° C. FOR ONE-HALF HOUR).

1.............	4.0010	0.4086	0.0003	0.4089	10.22	10 lead; 1,000° C. (one-half hour); 1 : 8 nitric acid (23 hours); 1 : 2.5 aqua regia (6 hours).
2.............	4.0013	.4087	.0002	.4089	10.22	
3.............	4.0013	.4067	.0020	.4087	10.22	
Average....	....	....	....	....	10.22	

SERIES V (1,000° C. FOR 4 HOURS).

1.............	4.0027	0.4059	0.0015	0.4074	10.18	20 lead; 1,000° C. (4 hours); 1 : 8 nitric acid (23 hours); 1 : 10 aqua regia (20 hours)
2.............	4.0015	.4068	.0007	.4075	10.18	
3.............	4.0021	.4043	.0009	.4052	10.12	
Average....	....	....	....	....	10.16	

8. EXPERIMENTS TO DETERMINE THE EFFECT OF RUTHENIUM.

Deville and Stas [9] found that ruthenium separates quantitatively with the iridium. The results given in Table 6 confirm this observation. The minimum value in this table is given as "minimum iridium + ruthenium," since part of the loss on melting may have been a loss of ruthenium.

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[9] Procès-verbaux, Comité International des Poids et Mesures, 1877, pp. 162, 191.

TABLE 6.—Effect of Ruthenium.

Alloy No. 119
$\begin{cases} \text{Maximum percentage of Ir} & = 9.96. \\ \text{Maximum percentage of Ru} & = 0.51. \\ \text{Maximum percentage of Ir+Ru} = 10.47. \\ \text{Minimum percentage of Ir+Ru} = 10.35. \end{cases}$

SERIES I.

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir. +Ru.	Percentage of Ir. +Ru.	Conditions.
1.............	g 4.0027	g 0.4177	g 0.0003	g 0.4180	10.44	10 lead; 1,000° C. (one-half hour); 1 : 8 nitric acid (19 hours); 1 : 2.5 aqua regia (6 hours).

SERIES II.

1.............	3.5021	0.3638	0.0001	0.3639	10.39	10 lead; 1,000° C. (4 hours); 1 : 8 nitric acid (25 hours); 1 : 10 aqua regia (24 hours).
2.............	3.5278	.3675	.0000	.3675	10.41	
Average....					10.40	

9. EXPERIMENTS TO DETERMINE THE EFFECT OF RHODIUM.

Deville and Stas[10] state that rhodium does not interfere in the iridium determination. The results of two series of analyses, although concordant, are higher than the maximum percentage of iridium in the alloy. In order to determine whether the apparently high results were caused by contamination with rhodium, the iridium from three experiments was examined for rhodium. In the first case the iridium was fused with zinc, the excess zinc removed with dilute hydrochloric acid, and the zinc-iridium alloy subjected to a lead fusion. In the second case the iridium was similarly treated, except that the zinc-iridium alloy was fused with potassium pyrosulphate. In both cases a quantity of rhodium not greater than o.oi per cent of the weight of the sample taken for analysis was extracted. In the third case the iridium was examined by spectrographic analysis. Rhodium was detected, but the quantity was very small. It was therefore concluded that the actual experimental values for iridium represented the true composition of the portion of the ingot which was prepared for analysis.

[10] Loc. cit., p. 162.

TABLE 7.—Effect of Rhodium.

Alloy No. 118
{Maximum percentage of Ir=5.06.
Minimum percentage of Ir=5.01.
Percentage of Rh   =5.04.

SERIES I.

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Weight of Ir, second determination.	Total weight of Ir.	Percentage of Ir.	Conditions.
	g	g	g	g		
1..............	4.0012	0.2044	0.0011	0.2055	5.14	10 lead; 1,000° C. (one-half hour); 1 : 8
2..............	4.0003	.2045	.0016	.2061	5.15	nitric acid (19 hours); 1 : 2.5 aqua regia
3..............	4.0021	.2058	.0015	.2073	5.18	(6 hours).
Average....					5.16	

SERIES II.

1..............	3.3941	0.1732	0.0009	0.1741	5.13	10 lead; 1,000° C. (4 hours); 1 : 8 nitric
2..............	3.3976	.1747	.0009	.1756	5.17	acid (25 hours); 1 : 10 aqua regia (24
Average....					5.15	hours).

10. EXPERIMENTS TO DETERMINE THE EFFECT OF PALLADIUM AND GOLD.

The results given in Table 8 show that the presence of palladium and gold in small percentages has no effect upon the determination of iridium. The two series of results likewise confirm the observation regarding the concentration of nitric acid. (See Table 1.)

TABLE 8.—Effect of Palladium and Gold.

Alloy No. 141
{Maximum percentage of Ir=5.35.
Minimum percentage of Ir=5.31.
Percentage of Pd   =3.07.
Percentage of Au   =2.32.

SERIES I (1 : 8 NITRIC ACID).

Experiment number.	Weight of sample.	Weight of Ir., first determination.	Percentage of Ir.	Conditions.
	g	g		
1..............	4.0003	0.2102	5.25	10 lead; 1,000° C. (1 hour); 1 : 8 nitric acid (22 hours);
2..............	4.0012	.2118	5.29	1 : 2.5 aqua regia (5 hours).
3..............	4.0015	.2122	5.30	
Average....			5.28	

SERIES II (1 : 4 NITRIC ACID).

1..............	4.0000	0.2116	5.29	10 lead; 1,000° C. (1 hour); 1 : 4 nitric acid (4 hours); 1 : 2.5
2..............	4.0017	.2112	5.28	aqua regia (5 hours).
3..............	4.0015	.2126	5.31	
Average....			5.29	

11. EXPERIMENTS ON THE EFFECT OF IRON.

Deville and Stas [11] found that about 85 per cent of the iron present in a 10 per cent iridium-90 per cent platinum alloy separated with the iridium and ruthenium during a lead fusion. The experiments given in Table 9 confirm this observation and show, in the case where iron is present in the alloy in an amount equal to 6 per cent of the iridium, that even a greater quantity of iron separates with the iridium. The analysis of some contact points containing approximately 5 per cent of iridium and 0.16 per cent of iron further confirm the observation that nearly all of the iron was weighed as iridium.

TABLE 9.—Effect of Iron.

Alloy No. 133 { Maximum percentage of Ir=4.75.
Minimum percentage of Ir=——.
Maximum percentage of Fe=0.31.

Experiment number.	Weight of sample.	Weight of Ir, first determination.	Percentage of Ir+Fe.	Fe in filtrates as per cent of sample.	Percentage Ir after removal of Fe.	Conditions.
	g	g				
1............	4.0024	0.2038	5.09	Trace.	....	10 lead; 1,000° C. (1 hour); 1 : 8 nitric acid (24 hours); 1 : 2.5 aqua regia (5 hours).
2............	4.0008	.2049	5.12	Absent.	4.65	
3............	4.0005	.2011	5.03	0.02	4.65	
4............	4.0021	.2016	5.04	.01	4.71	
5............	4.0016	.2032	5.08	.005	4.72	
Average....	....	....	5.07	....	4.68	

NOTE.—The iron determined by colorimetric analysis in a separate sample was 0.31 per cent.

The determination of the total iron in the alloy was made by a colorimetric analysis as follows: One gram of the alloy was dissolved in aqua regia. The solution was evaporated with hydrochloric acid three times to destroy nitric acid present. Two cubic centimeters of concentrated hydrochloric acid was added and the volume made 200 cc with water. Fifty-cubic-centimeter portions, equivalent to one-fourth-gram samples of the alloy, were taken for analysis. Forty milligrams of ammonium alum was added to each solution. The boiling solutions were made slightly ammoniacal. The precipitates of iron and aluminum hydroxide were filtered from the solutions, redissolved, and twice reprecipitated to completely remove platinum and iridium. The final precipitate was dissolved in 1 cc of concentrated hydrochloric acid, the solution diluted slightly, and filtered into colorimetric tubes. Five cubic centimeters of a 5 per cent ammonium thiocyanate solution

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[11] Procès-verbaux, Comité International des Poids et Mesures, 1877, p. 177.

was added and the solutions diluted to about 50 cc. By titrating the blank determinations on the reagents used with a standard ferric chloride solution (0.1 mg per cc) the quantity of iron in the alloy samples was found.

The quantity of iron remaining in the filtrates from the iridium analysis was determined in a similar manner. The combined filtrates after the removal of lead as sulphate were diluted to 500 cc. Portions, 150 cc in volume, were taken for analysis. These solutions were analyzed in two ways: First, according to the procedure given above; and, second, by first removing all the platinum present with hydrogen sulphide.

It is thus possible to make a correction for iron in the iridium by determining on a separate sample the total iron present in the alloy and the iron remaining in the filtrates from the iridium analysis. Since it is not always possible to make the correction in this way, a procedure is offered, suggested by W. H. Swanger, of this laboratory, by which the iron can be separated from the iridium. This procedure involves several quantitative transfers, careful manipulation, and considerable time. The method used to separate the iron was as follows: The iridium was quantitatively transferred to a quartz crucible. Fifteen grams of pure zinc was added and melted over a Bunsen burner, using pure fused zinc chloride as a cover. The fusion was maintained at dull red heat for 15 minutes, and the melt frequently stirred with a slender graphite rod to insure complete solution of the iridium in the zinc. After cooling, the crucible with its contents was placed in a 250 cc beaker and digested with dilute hydrochloric acid. The material adhering to the graphite rod was removed by dilute hydrochloric acid and added to the main solution. When the excess zinc was dissolved, the insoluble portion, consisting of a zinc-iridium alloy, coagulated, leaving a clear supernatant solution. This was decanted through a filter and the residue washed by decantation with hot dilute ammonium chloride solution. The filter carrying a small portion of the residue was ignited in a porcelain crucible to which the main portion of the zinc-iridium alloy was then added and dried on the steam bath. The material thus dried was fused with 15 g of potassium pyrosulphate, the crucible being covered with a perforated quartz lid. The temperature of the fused pyrosulphate was maintained between 650 and 750° C. for about one hour. After cooling, the melt was leached with 100 cc of water containing 2 cc of sulphuric acid. The residue, consisting probably of iridium oxide, was caught on a double filter and washed with hot dilute ammonium

chloride solution. The filters with the iridium were dried not quite completely in a porcelain crucible. To avoid loss because of a tendency to deflagrate, the filters were charred in hydrogen before igniting in air. The iridium was next transferred to a filter, washed with hot water, and ignited in a platinum crucible. Silica was removed by a treatment with hydrofluoric and sulphuric acids. The iridium was transferred again to a filter, washed thoroughly with hot water, ignited in a porcelain crucible, reduced in an atmosphere of hydrogen, and weighed. The results obtained by this separation are given in the sixth column in Table 9. In this table the "minimum iridium percentage" is lacking. This is due to the fact that the alloy was cast in graphite with a small mechanical loss in casting, making it impossible to ascertain the amount of iridium volatilized.

To determine whether this procedure could be conducted without loss of iridium, experiments were made with samples of iridium containing no iron. The samples weighed 0.1940, 0.1945, and 0.1938 g, and the recoveries were 0.1951, 0.1933, and 0.1937 g, respectively.

12. ANALYSIS OF AN ALLOY CONTAINING A SMALL AMOUNT OF IRIDIUM.

Three analyses were made of an alloy calculated to contain 0.084 per cent of iridium. The samples weighed 5 g, and the results were 0.070, 0.068, and 0.066 per cent, with an average of 0.068 per cent. The values are seen to be slightly low. It was in the analysis of this alloy early in the stage of experimentation that iridium was observed to be present in the aqua regia solution. The iridium was detected qualitatively [12] in the filtrate, after the removal of the platinum by formic acid.[13] The filtrate, to which a small quantity of concentrated sulphuric acid had been added, was evaporated until fumes of sulphuric acid escaped, cooled somewhat, treated with a few drops of nitric acid, and the solution again heated to the fuming point. At this point a blue color developed, characteristic of the presence of iridium.

13. EXPERIMENTS TO DETERMINE THE QUANTITY OF INSOLUBLE MATERIAL INTRODUCED INTO THE IRIDIUM DURING THE ANALYSIS.

Five experiments were conducted, two with 20 g of granular test lead each, and three with 40 g. The actual conditions of the analysis of an alloy were duplicated. The 20 g portions each

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[12] Qualitative Chemical Analysis, Fresenius, English Translation of 17th German ed., p. 377

[13] Although formic acid can be used to precipitate other metals of the platinum group, it is seldom possible to precipitate iridium completely by means of reducing agents.

gave an insoluble residue of 0.0006 g, while the 40 g portions each gave a residue of 0.0005 g. The correction, 0.0005 g, was applied to the weight of the iridium in all of the analyses reported in this paper.

14. EXPERIMENTS TO DETERMINE THE LOSS IN WEIGHT OF CRYSTALLINE IRIDIUM DURING IGNITION IN AIR.

Two samples of crystalline iridium obtained in the course of an analysis and weighing 0.3595 and 0.4105 g, respectively, were heated in open porcelain crucibles with the full heat of a Tirrill burner. At the end of 1, 3, 4, and 8 hours, respectively, the samples of iridium were reduced in hydrogen and weighed. The weights of the first sample were 0.3595, 0.3594, 0.3593, and 0.3593 g and of the second 0.4105, 0.4103, 0.4102, and 0.4101 g, showing that in the time required for ignition in the regular analysis, namely, about one hour, there would be no significant loss in weight.

15. EXPERIMENTS TO DETERMINE THE EFFECT OF HYDROGEN ON THE WEIGHT OF CRYSTALLINE IRIDIUM.

A porcelain boat containing 0.4465 g of crystalline iridium, obtained in one of the analyses, was heated in a hard glass tube to a temperature of about 750° C. by an electric furnace for one hour in a current of pure dry hydrogen and cooled in this gas. The iridium was again heated in hydrogen, the hydrogen displaced for 15 minutes by pure dry nitrogen, and the metal cooled in the latter gas. In each case the iridium weighed 0.4466 g.

16. SPECTROSCOPIC EXAMINATION OF IRIDIUM OBTAINED IN THE ANALYSES.

The arc spectra [14] of 11 samples of iridium were obtained by burning the metal between electrodes of pure copper. The iridium in two of the samples had been examined chemically for rhodium and platinum by fusing with zinc, etc., as described in a previous paragraph. These two as well as three other samples contained no platinum or lead. In the other six samples platinum and lead were reported as doubtful, and, therefore, they were not present in sufficient quantity to affect the determination. No zinc was found in the iridium which had been fused with zinc and subsequently with potassium pyrosulphate.

[14] Meggers, Kiess, and Stimson, B. S. Sci. Papers No. 444.

VI. DISCUSSION OF THE RESULTS OBTAINED.

The experimental data show that the results have a tendency to be somewhat low, and that the error is variable in the determination of iridium by the method of Deville and Stas. In the majority of cases studied the error was less than 0.05 per cent, calculated on the basis of the sample taken. Such an error may probably be disregarded, but when the greatest accuracy is desired a recovery should be made.

The results of the analyses further show that the original Deville and Stas procedure can be greatly shortened. The time of the lead fusion can be reduced from four hours to one hour. With 1 : 4 nitric acid concentration the time required for complete disintegration of the lead button is shortened to two hours, while the time necessary for solution of the lead-platinum alloy is reduced to one and one-half hours when the concentration of aqua regia 1 : 2.5 is used. Experiments show that it is not necessary to use a quantity of lead greater than 10 times the weight of the alloy.

The data indicate that palladium, gold, and rhodium have no effect upon the iridium determination, whereas ruthenium separates quantitatively with the iridium. Iron separates nearly quantitatively with the iridium, but can be separated from it by a series of treatments, the description of which has been given. Nearly all commercial platinum, and especially platinum-iridium alloys, are liable to be contaminated with iron. The correction for iron is therefore important.

VII. PROPOSED MODIFIED PROCEDURE.

The following modification of the Deville and Stas method is recommended:

1. LEAD FUSION.

Fuse the carefully sampled platinum alloy with 10 times its weight of granular test lead for a period of one hour at a temperature of about 1,000° C. A covered crucible, whose outside dimensions are 1 ½ inches in diameter and 2 ½ inches in height, machined from Acheson graphite, is suitable for fusions using from 20 to 40 g of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium has largely settled to the bottom of the crucible. The crucible is best heated in an electric furnace.

2. DISINTEGRATION WITH NITRIC ACID.

Brush the cooled lead ingot free from carbon with a camel's-hair brush, and place it in a beaker. Add nitric acid of the concentration 1 volume of acid (sp. gr. 1.42) to 4 volumes of water, using 1 cc of acid per gram of lead. Place the beaker on the steam bath or on a hot plate which maintains the temperature of the solution at about 85° C. Disintegration of the lead ingot is usually complete in about two hours, leaving a rather voluminous grayish black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of a 9 cm paper of fine texture, such as S. & S. No. 589 blue ribbon filter, on which is superimposed a 7 cm paper of looser texture, such as No. 589 black ribbon. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make it easier to detect the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Any particles of the residue collect at the center of the bottom of the flask. Return the filters to the beaker without ignition.

3. SOLUTION OF THE LEAD-PLATINUM ALLOY BY AQUA REGIA.

Add in order 15 cc of water, 5 cc of hydrochloric acid (sp. gr. 1.18), and 0.8 cc nitric acid (sp. gr. 1.42) for each gram of platinum alloy taken. Heat the solution in the beaker on the steam bath or on a hot plate which maintains the temperature at about 85° C. The lead-platinum alloy is usually completely dissolved within one and one-half hours. Dilute the solution with twice its volume of water and filter through a double filter, similar to the one used for the lead nitrate solution. The iridium, insoluble in the aqua regia, is in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this the interior of the beaker is wiped with a piece of filter paper to collect any metal adhering to the sides. Then by whirling a small quantity of water in the beaker any iridium remaining gravitates toward one place, whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dilute hydrochloric acid (1:100), and lastly with hot water. The chloroplatinic acid

filtrate and washings should be examined for iridium which may have passed through the filters in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

4. IGNITION AND REDUCTION OF THE IRIDIUM.

Place the washed filters and iridium in a porcelain crucible and dry before igniting in air. After the destruction of the filter paper ignite the iridium strongly with the full heat of a Tirrill burner. After all carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube is preferred). After five minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

In commercial analysis no effort is made to correct the weight of iridium for small amounts of ruthenium. Correction, if desired, can be made according to the original directions of Deville and Stas. The correction for iron can be made according to the procedure given with the discussion of the analysis of the iron-iridium-platinum alloy.

WASHINGTON, October 8, 1923.